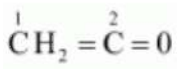
NCERT Solutions for Class-XI Chemistry

Chapter-12
NCERT Chemistry Class 11

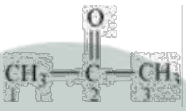
1. What are hybridisation states of each carbon atom in the following compounds?
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

1. (1) 

Câ€“1 is sp^2 hybridised.
Câ€“2 is sp hybridised.

(2) 

Câ€“1 is sp^3 hybridised.
Câ€“2 is sp^2 hybridised.
Câ€“3 is sp^2 hybridised.

(3) 

Câ€“1 and Câ€“3 are sp^3 hybridised.
Câ€“2 is sp^2 hybridised.

(4) 

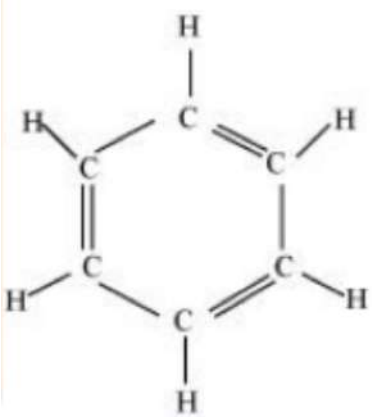
Câ€“1 is sp^2 hybridised.
Câ€“2 is sp^2 hybridised.
Câ€“3 is sp hybridised.

(5) C_6H_6

All the 6 carbon atoms in benzene are sp 2 hybridised.

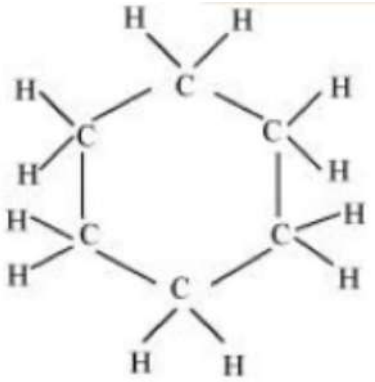
2. Indicate the ÃÆ’ and Ãâ,¬ bonds in the following molecules:
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2 = C = CH_2$, CH_3NO_2, HCONHCH$_3$

2. The structure of C_6H_6 is shown below.



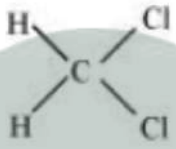
Single bond contains only one sigma bond and double bond contains one sigma and one pi bond. In this structure, nine single bonds and three double bonds are present. So, there are 12σ and 3π bonds present.

The structure of C_6H_{12} is shown below.



In this structure, eighteen single bonds are present. So, there are only 18σ bonds present.

The structure of CH_2Cl_2 is shown below.

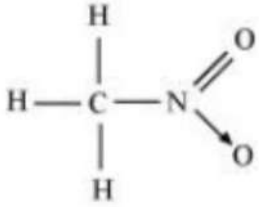


In this structure, four single bonds are present. So, there are only 4σ bonds present.

The structure of $CH_2=C=CH_2$ is shown below.

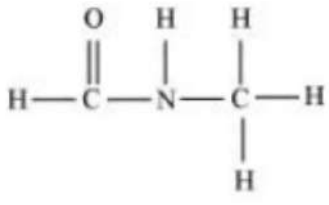
In this structure, four single bonds and two double bonds are present. So, there are 6σ and 2π bonds present.

The structure of CH_3NO_2 is shown below.



In this structure, five single bonds and one double bond are present. So, there are 6σ and 1π bonds present.

The structure of $HCONHCH_3$ is shown below.

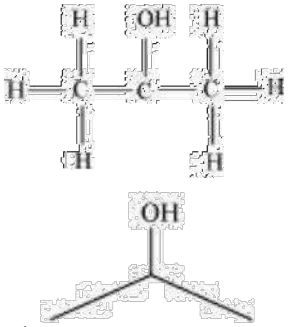


In this structure, seven single bonds and one double bond are present. So, there are 8σ and 1π bonds present.

3. Write bond line formulas for: Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

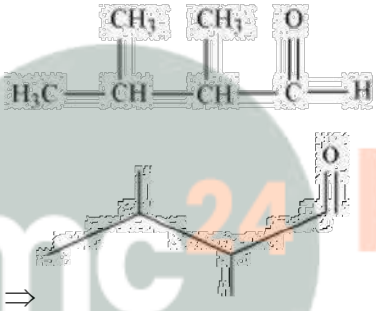
3. The bond line formulae of the given compounds are:

(a) Isopropyl alcohol



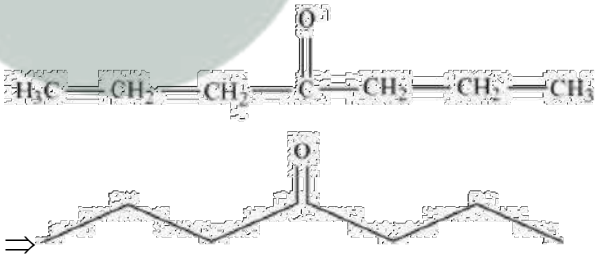
$\Rightarrow$

(b) 2, 3-dimethyl butanal



$\Rightarrow$

(c) Heptan-4-one



$\Rightarrow$

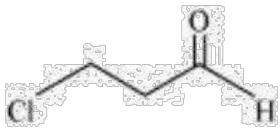
4. Give the IUPAC names of the following compounds:

(a)

(b)

(c)

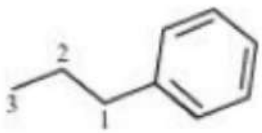
(d) 

(e) 

(f) Cl_2CHCH_2OH

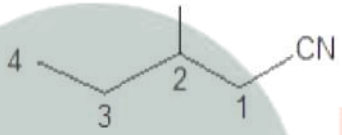
4.

(a)



In this structure, the longest chain of carbon contains 3 carbon atoms and one phenyl group is present. So, the IUPAC name is 1-phenyl propane.

(b)

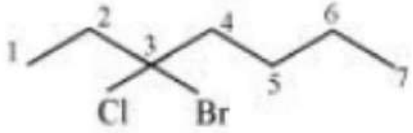


In this structure, the longest chain of carbon contains four carbon atoms. Also, one methyl and one cyanide groups are attached with carbon-2 and carbon-1 respectively. So, the IUPAC name is 2-methyl-1-cyanobutane.

(c)

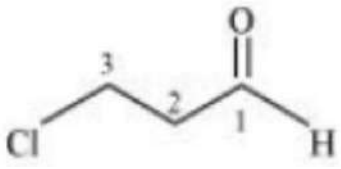
In this structure, the longest chain of carbon contains 7 carbon atoms and 2 methyl are positioned at carbon-2 and carbon-5. So, the IUPAC name of the compound is 2, 5-dimethyl heptane.

(d)



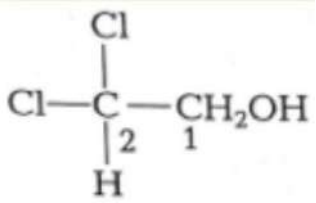
In this structure, the longest chain of carbon contains 7 carbon atoms. Also, 1 chloro and 1 bromo groups are present at carbon-3. So, the IUPAC name of the compound is 3-bromo-3-chloroheptane.

(e)



In this structure, the longest chain of carbon contains 3 carbon atoms. Also, 1 aldehyde and 1 chloro functional groups are present at carbon-1 and carbon-3 respectively. So, the IUPAC name of the compound is 3-chloropropanal.

(f)



In this structure, the longest chain of carbon contains 2 carbon atoms. Also, 1 alcohol and 2 chloro functional groups are present at carbon- 1 and carbon-2 respectively. So, the IUPAC name of the compound is 2,2-dichloro-1-ethanol.

5. Which of the following represents the correct IUPAC name for the compounds concerned? (a) 2,2- Dimethylpentane or 2-Dimethylpentane (b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane (c) 2-Chloro-4- methylpentane or 4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-1-yne

5. (a) The prefix diin the IUPAC name indicates that two identical substituent groups are present in the parent chain. Since two methyl groups are present in the C-2 of the parent chain of the given compound, the correct IPUAC name of the given compound is 2, 2-dimethylpentane.

(b) Locant number 2, 4, 7 is lower than 2, 5, 7. Hence, the IUPAC name of the given compound is 2, 4, 7- trimethyloctane.

(c) If the substituents are present in the equivalent position of the parent chain, then the lower number is given to the one that comes first in the name according to the alphabetical order. Hence, the correct IUPAC name of the given compound is 2-chloro-4-methylpentane.

(d) Two functional groups - alcoholic and alkyne - are present in the given compound. The principal functional group is the alcoholic group. Hence, the parent chain will be suffixed with ol. The alkyne group is present in the C-3 of the parent chain. Hence, the correct IUPAC name of the given compound is But-3-yn-1-ol.

6. Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H-COOH (b) CH_3COCH_3 (c) $H-CH=CH_2$

6. The following are the first 5 members of each homologous series, starting with the given compounds:

(a) H-- COOH: Methanoic acid

CH_3-COOH : Ethanoic acid

CH_3-CH_2-COOH : Propanoic acid

$CH_3 - CH_2 - CH_2 - COOH$: Butanoic acid

$CH_3 - CH_2 - CH_2 - CH_2 - COOH$: Pentanoic acid

(b) CH_3COCH_3 : Propanone

$CH_3COCH_2CH_3$: Butanone

$CH_3COCH_2CH_2CH_3$: Pentan - 2 - one

$CH_3COCH_2CH_2CH_2CH_3$: Hexan - 2 - one

$CH_3COCH_2CH_2CH_2CH_2CH_3$: Heptan - 2 - one

(c) $H - CH = CH_2$: Ethene

$CH_3 - CH = CH_2$: Propene

$CH_3 - CH_2 - CH = CH_2 : 1 -$ Butene

$CH_3 - CH_2 - CH_2 - CH = CH_2 : 1$ - Pentene

$CH_3 - CH_2 - CH_2 - CH_2 - CH = CH_2 : 1 -$ Hexene

7. Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

(a) 2,2,4-Trimethylpentane

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

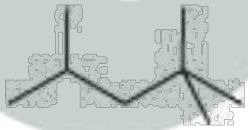
(c) Hexanedial

7. (a) 2, 2, 4-trimethylpentane

Condensed formula:

$(CH_3)_2CHCH_2C(CH_3)_3$

Bond line formula:

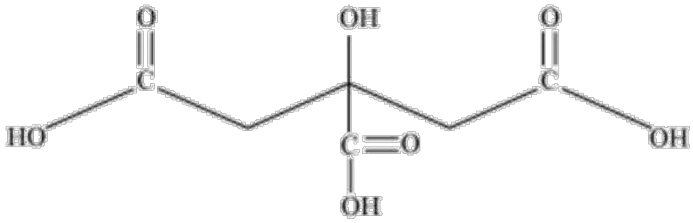


(b) 2-hydroxy-1, 2, 3-propanetricarboxylic acid

Condensed Formula:

$(COOH)CH_2C(OH)(COOH)CH_2(COOH)$

Bond line formula:



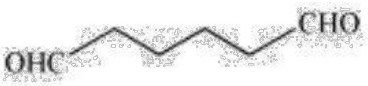
The functional groups present in the given compound are carboxylic acid (-COOH) and alcoholic (-OH) groups.

(c) Hexanedial

Condensed Formula:

$(CHO)(CH_2)_4(CHO)$

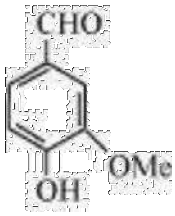
Bond line Formula:



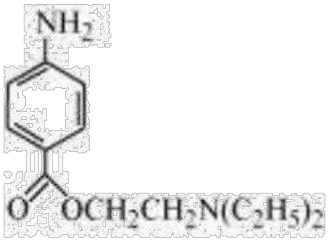
The functional group present in the given compound is aldehyde (-CHO).

8. Identify the functional groups in the following compounds

(a)



(b)



(c)

8. (a) In the given compound, aldehyde (-CHO), hydroxyl (-OH) and methoxy (-OMe) functional groups are present.

(b) In the given compound, amino $\left(-NH_2\right)$, ketone $\left(C=O\right)$, diethylamine $\left(N(C_2H_5)_2\right)$ functional groups are present.

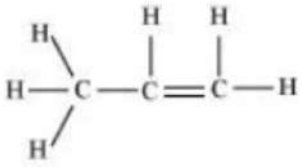
(c) In the given compound, nitro group $\left(-NO_2\right)$ and $C=C$ double bond are present.

9. Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?

9. NO_2group is an electron-withdrawing group. Hence, it shows -I effect. By withdrawing the electrons toward it, the NO_2group decreases the negative charge on the compound, thereby stabilising it. On the other hand, ethyl group is an electron-releasing group. Hence, the ethyl group shows +I effect. This increases the negative charge on the compound, thereby destabilising it. Hence, $O_2NCH_2CH_2O^-$ is expected to be more stable than $CH_3CH_2O^-$.

10. Explain why alkyl groups act as electron donors when attached to a Ãâ,¬ system.

10. When an alkyl group is linked to a π system, the process of hyperconjugation causes it to act as an electron-donor group. Let us use propene as an example to better comprehend this topic.



The sigma electrons of an alkyl group's $C-H$ bond are delocalised during hyperconjugation. This group is directly connected to an unsaturated system's atom. The delocalisation happens as a result of a partial overlap of a sp^3 sigma bond orbital with an empty p orbital of the pi bond of a nearby carbon atom's bond.

11. Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) C_6H_5OH

(b) $C_6H_5NO_2$

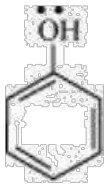
(c) $CH_3CH = CH$ â€“ CHO

(d) C_6H_5CHO

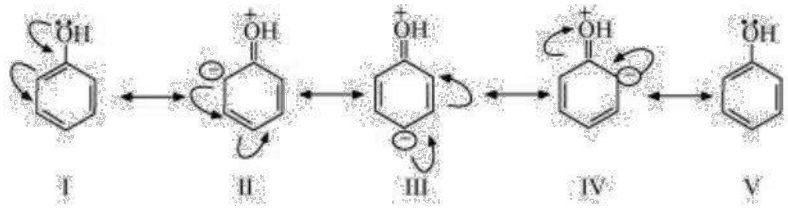
(e) $C_6H_5-\overset{+}{C}H_2$

(f) $CH_3CH=CH\overset{+}{C}H_2$

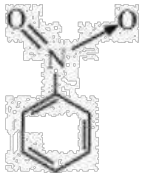
11. (a) The structure of C_6H_5OH is:



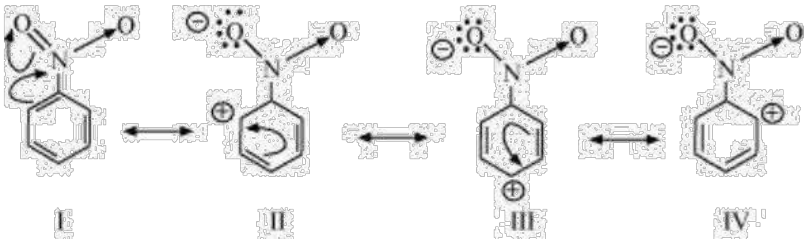
The resonating structures of phenol are represented as:



(b) The structure of $C_6H_5NO_2$ is:

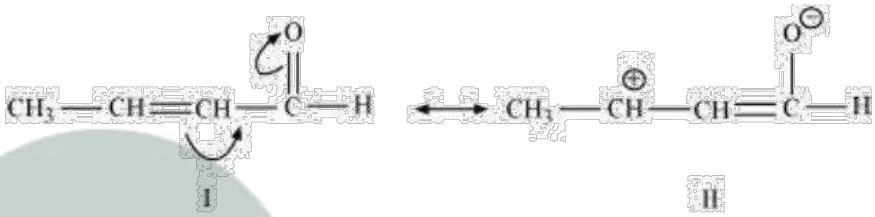


The resonating structures of nitro benzene are represented as:



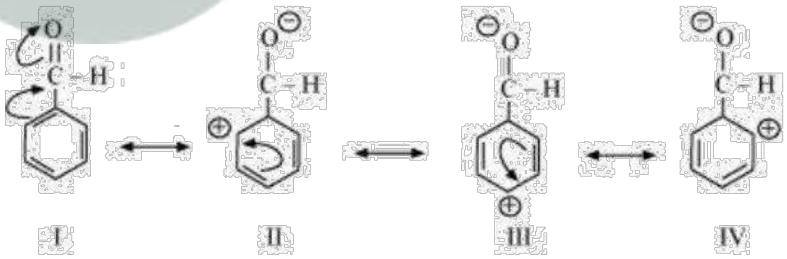
(c) $CH_3CH=CH-CHO$

The resonating structures of the given compound are represented as:



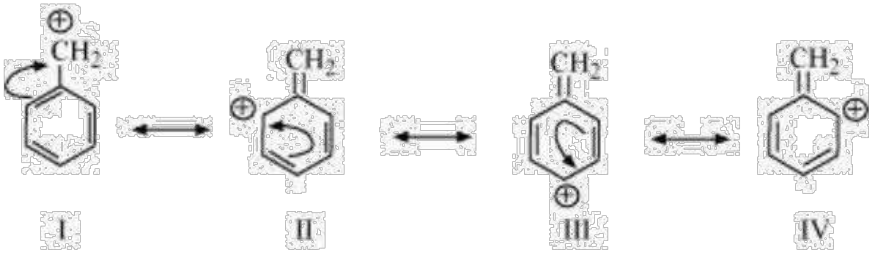
(d) The structure of C_6H_5CHO is:

The resonating structures of benzaldehyde are represented as:



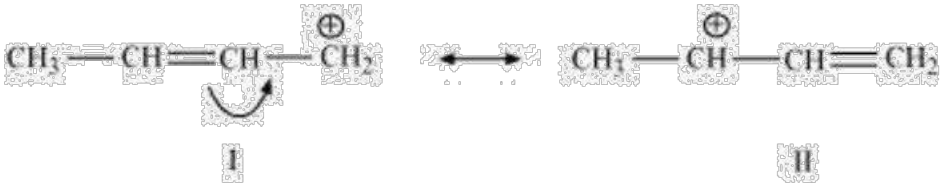
(e) $C_6H_5CH_2$Ã¢Å"¢

The resonating structures of the given compound are:



(f) CH_3 CH=CH CH_2Ã¢Å"¢

The resonating structures of the given compound are:



I II

12. What are electrophiles and nucleophiles? Explain with examples.

12. An electrophile is a reagent that removes a pair of electrons. In other words, an electrophile $\left(E^{+}\right)$is a reagent that seeks electrons. Electrophiles are electron deficient and receiver of an electron pair. Electrophiles include carbocations and $\left(CH_3CH_2^{+}\right)$ neutral compounds with functional groups such as the carbonyl group.

A reagent that produces an electron pair is known as a nucleophile. A nucleusseeking reagent is referred to as a nucleophile (Nu:).

For instance, OH^{-}, NC^{-}, carbanions $\left(R_3C^{-}\right)$, and so on.

Because of the presence of a lone pair, neutral molecules such as water and ammonia also serve as nucleophiles.

13. Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(a) $CH_3COOH + \mathbf{HO^{-}} \longrightarrow CH_3COO^{-} + H_2O$

(b) $CH_3COCH_3 + \mathbf{\overset{-}{C}N} \longrightarrow \left(CH_3\right)_2 C\left(CN\right) + \left(OH\right)$

(c) $\mathbf{C_6H_5} + CH_3\overset{+}{C}O \longrightarrow C_6H_5COCH_3$

13. Electrophiles are electron-deficient species and can receive an electron pair. On the other hand, nucleophiles are electron-rich species and can donate their electrons.

(a) $CH_3COOH + \mathbf{HO^{-}} \longrightarrow CH_3COO^{-} + H_2O$

Here, HOâ€“ acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.

(b) $CH_3COCH_3 + \mathbf{\overset{-}{C}N} \longrightarrow \left(CH_3\right)_2 C\left(CN\right) + \left(OH\right)$

Here, â€“CN acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.

(c) $\mathbf{C_6H_5} + CH_3\overset{+}{C}O \longrightarrow C_6H_5COCH_3$

Here, $CH_3\overset{+}{C}O$ acts as an electrophile as it is an electron-deficient species.

14. Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^{-} \rightarrow CH_3CH_2SH + Br^{-}$

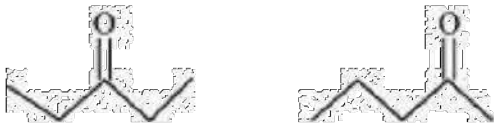
(b) $(CH_3)_2C{=}CH_2 + HCl \rightarrow (CH_3)_2ClC\text{-}CH_3$

(c) $CH_3CH_2Br + HO^{-} \rightarrow CH_2{=}CH_2 + H_2O + Br^{-}$

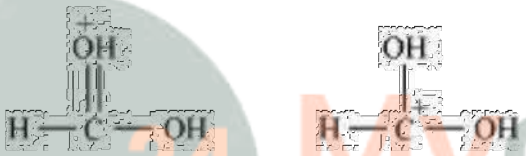
(d) $(CH_3)_3C\text{-}CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$

14. (a) The given reaction is a type of a substitution reaction because the bromine group in bromoethane is substituted by thionyl group.
(b) The given reaction is a type of an addition reaction because two reactant molecules react to produce a single product.
(c) The given reaction is a type of an elimination reaction because hydrogen and bromine are eliminated by bromoethane in order to produce ethene.
(d) Substitution takes place in this reaction, followed by atom and atom group rearrangement.

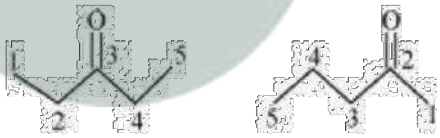
15. What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?

(a) 

(b) 

(c) 

15. (a) Compounds having the same molecular formula but with different structures are called structural isomers. The given compounds have the same molecular formula but they differ in the position of the functional group (ketone group).

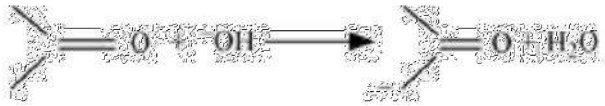


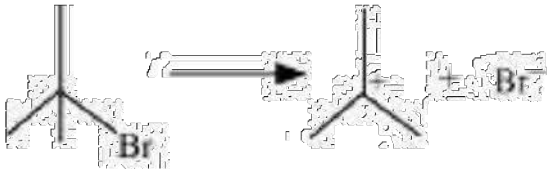
In structure I, ketone group is at the C-3 of the parent chain (hexane chain) and in structure II, ketone group is at the C-2 of the parent chain (hexane chain). Hence, the given pair represents structural isomers.
(b) Compounds having the same molecular formula, the same constitution, and the sequence of covalent bonds, but with different relative position of their atoms in space are called geometrical isomers.

In structures I and II, the relative position of Deuterium (D) and hydrogen (H) in space are different. Hence, the given pairs represent geometrical isomers.
(c) The given structures are canonical structures or contributing structures. They are hypothetical and individually do not represent any real molecule. Hence, the given pair represents resonance structures, called resonance isomers.

16. For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O-OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$

(b) 

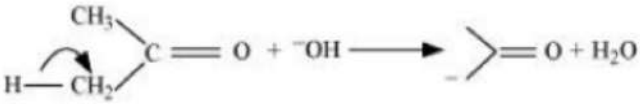
(c) 

(d) 

16. (a) The bond cleavage can be illustrated using curved arrows to show the electron flow of the given reaction as

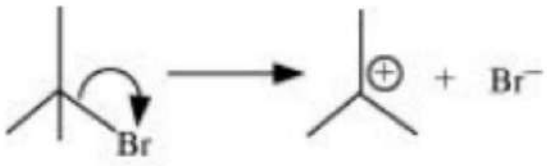
As one of the shared pairs in a covalent bond travels with the connected atom, it is an example of homolytic cleavage. A free radical is produced as a reaction intermediate.

(b) The bond cleavage can be illustrated using curved arrows to show the electron flow of the given reaction as



It is an example of heterolytic cleavage because the bond breaks in such a way that the shared pair of electrons stay with the carbon of propanone. The reactive intermediate created is carbanion.

(c) The bond cleavage can be illustrated using curved arrows to show the electron flow of the given reaction as



It is an example of heterolytic cleavage because the bond breaks in such a way that the bromine ion retains the shared pair of electrons. A carbocation is produced as a reaction intermediate.

(d) The bond cleavage can be illustrated using curved arrows to show the electron flow of the given reaction as

The bond breaks in such a way that the shared pair of electrons stays with one of the fragments, resulting in a heterolytic cleavage. A carbocation is created as an intermediate.

17. Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

17. Inductive effect

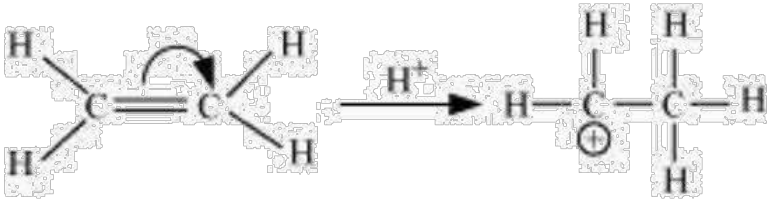
The permanent displacement of sigma (ÃÆ') electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present, is called inductive effect.

Inductive effect could be + I effect or - I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess - I effect. For example,

When an atom or group attracts electrons towards itself less strongly than hydrogen, it is said to possess + I effect. For example,

Electrometric effect

It involves the complete transfer of the shared pair of Ãâ,¬ electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent. For example,



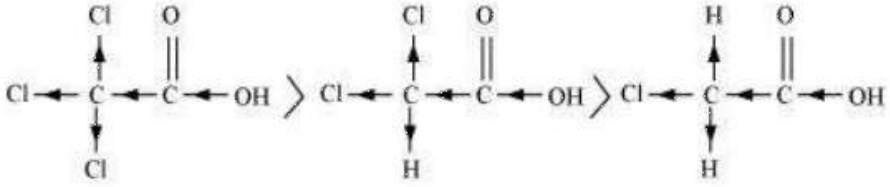
Electrometric effect could be + E effect or - E effect.

+ E effect: When the electrons are transferred towards the attacking reagent

-E effect: When the electrons are transferred away from the attacking reagent

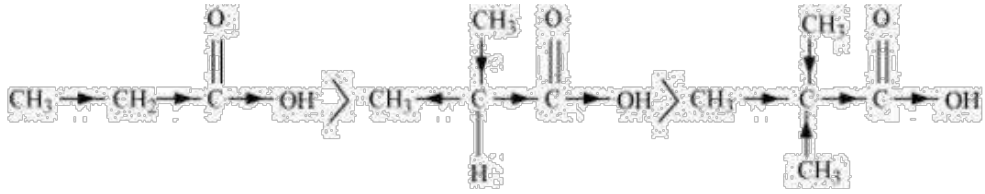
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

The order of acidity can be explained on the basis of Inductive effect (- I effect). As the number of chlorine atoms increases, the - I effect increases. With the increase in - I effect, the acid strength also increases accordingly.



(b) $CH_3CH_2COOH > (CH_3)_2 CHCOOH > (CH_3)_3 C.COOH$

The order of acidity can be explained on the basis of inductive effect (+ I effect). As the number of alkyl groups increases, the + I effect also increases. With the increase in + I effect, the acid strength also increases accordingly.



18. Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation

(b) Distillation

(c) Chromatography

18. (a) Crystallisation: It is one of the most widely used methods for purifying solid chemical molecules.

Principle: The differential in the solubilities of the compound and the impurities in a solvent. The impure substance dissolves in the solvent, which is only sparingly soluble at ambient temperature but completely soluble at higher temperatures. The solution is concentrated until it is virtually saturated. When the solution is cooled, the pure compound crystallises and is extracted by filtration.

Pure aspirin, for example, is created by recrystallising crude aspirin. 2 - 4 g of crude aspirin is dissolved in approximately 20 mL of ethyl alcohol. To ensure complete decomposition, the solution is heated.

(b) Distillation: This approach is used to separate volatile liquids from nonvolatile contaminants or a mixture of those liquids with a large enough difference in boiling points.

Principle: It works on the principle that liquids with different boiling points vapourize at different temperatures. The vapours are then cooled, and the liquids that form are separated.

For example: Distillation can be used to separate a combination of chloroform and aniline. The mixture is placed in a condenser-equipped round bottom flask. After that, it is heated. Because chloroform is more volatile, it vaporizes first and enters the condenser. The vapours condense in the condenser, and chloroform trickles down. Aniline is left in the round bottom flask.

(c) Chromatography: It is one of the most effective technologies for organic chemical separation and purification. Principle: The differential in movement of separate

components of a mixture through the stationary phase under the influence of the mobile phase is the basis for the principle.

Example: Chromatography, can separate a combination of red and blue ink. On the chromatogram, a drop of the combination is inserted. The component of the ink that is less adsorbed on the chromatogram travels with the mobile phase, whereas the component that is more adsorbed remains stationary.

19. Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

19. Fractional crystallisation is the method used for separating two compounds with different solubilities in a solvent S. The process of fractional crystallisation is carried out in four steps.

(a) Preparation of the solution: The powdered mixture is taken in a flask and the solvent is added to it slowly and stirred simultaneously. The solvent is added till the solute is just dissolved in the solvent. This saturated solution is then heated.

(b) Filtration of the solution: The hot saturated solution is then filtered through a filter paper in a China dish.

(c) Fractional crystallisation: The solution in the China dish is now allowed to cool. The less soluble compound crystallises first, while the more soluble compound remains in the solution. After separating these crystals from the mother liquor, the latter is concentrated once again. The hot solution is allowed to cool and consequently, the crystals of the more soluble compound are obtained.

(d) Isolation and drying: These crystals are separated from the mother liquor by filtration. Finally, the crystals are dried.

20. What is the difference between distillation, distillation under reduced pressure and steam distillation?

20. The differences between distillation, reduced pressure distillation, and steam distillation are shown below.

Distillation: It is used to purify chemicals that are related with non-volatile impurities or liquids that do not disintegrate when heated. In other words, distillation is used to separate volatile liquids from nonvolatile contaminants or a mixture of such liquids with significant boiling point difference. This process separates a mixture of fuel and kerosene.

Reduced pressure distillation: This procedure is used to purify a liquid that decomposes when heated. Under reduced pressure, the liquid will boil at a lower temperature than its boiling point and so will not decompose.

This process is used to purify glycerol. At a temperature of $593\ K$, it boils with decomposition. It boils at $453\ K$ without breakdown at a lower pressure.

Steam distillation: It is used to purify an organic molecule that is steam volatile and water immiscible. The compound is heated by passing steam, and the steam is condensed to water. After some time, the water-liquid mixture begins to boil and flows through the condenser. A separating funnel is then used to separate this condensed mixture of water and liquid.

A solution of water and aniline can be separated by this method.

21. Discuss the chemistry of Lassaigne's test.

21. Lassaigne's test

This test is employed to detect the presence of nitrogen, sulphur, halogens, and phosphorous in an organic compound. These elements are present in the covalent form in an organic compound. These are converted into the ionic form by fusing the compound with sodium metal.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S$$

$$Na + X \xrightarrow{\Delta} \underset{(X = Cl, Br, I)}{NaX}$$

The cyanide, sulphide, and halide of sodium formed are extracted from the fused mass by boiling it in distilled water. The extract so obtained is called Lassaigne's extract. This Lassaigne's extract is then tested for the presence of nitrogen, sulphur, halogens, and phosphorous.

(a) Test for nitrogen

Chemistry of the test

In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$$6CN^- + Fe^{2+} \longrightarrow \left[Fe(CN)_6\right]^{4-}$$

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue colour}}{Fe_4\left[Fe(CN)_6\right]_3.xH_2O}$$

(b) Test for sulphur

(i) $\text{Lassaigne's extract} + \text{Lead acetate} \xrightarrow{\text{acetic acid}} \text{Black precipitate}$

Chemistry of the test

In the Lassaigne's test for sulphur in an organic compound, the sodium fusion extract is acidified with acetic acid and then lead acetate is added to it. The precipitation of lead sulphide, which is black in colour, indicates the presence of sulphur in the compound.

$$S^{2-} + Pb^{2+} \longrightarrow \underset{(Black)}{PbS}$$

(ii) Lassaigne's extract + Sodium nitroprusside $\longrightarrow$ Violet colour

Chemistry of the test

The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour also indicates the presence of sulphur in the compound.

$$S^{2-} + \left[Fe(CN)_5 NO\right]^{2-} \longrightarrow \underset{(Violet)}{\left[Fe(CN)_5 NOS\right]^{-4}}$$

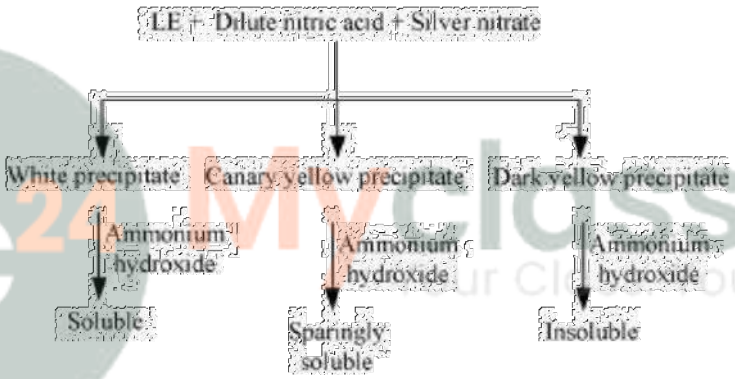
If in an organic compound, both nitrogen and sulphur are present, then instead of NaCN, formation of NaSCN takes place.

Na + C + N + S Ã¢â€' NaSCN

This NaSCN (sodium thiocyanate) gives a blood red colour. Prussian colour is not formed due to the absence of free cyanide ions.

$$Fe^{3+} + SCN^{-} \longrightarrow \underset{(Blood\ red)}{\left[Fe(SCN)\right]^{2+}}$$

(c) Test for halogens



Chemistry of the test

In the Lassaigne's test for halogens in an organic compound, the sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$$X^{-} + Ag^{+} \longrightarrow \underset{(X=Cl, Br, I)}{AgX}$$

If nitrogen and sulphur both are present in the organic compound, then the Lassaigne's extract is boiled to expel nitrogen and sulphur, which would otherwise interfere in the test for halogens.

22. Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method.

22. In the Dumas method, a specified amount of a nitrogen-containing organic molecule is burned strongly with an excess of copper oxide in a carbon dioxide atmosphere to yield free nitrogen as well as carbon dioxide and water.

The process can also yield traces of nitrogen oxides, which can be converted to dinitrogen by passing the gaseous mixture over a heated copper gauge. The dinitrogen generated is collected over a potassium hydroxide aqueous solution. At room

temperature and atmospheric pressure, the volume of nitrogen generated is then measured.

Kjeldahl's method, on the other hand, involves heating a known quantity of a nitrogen-containing organic molecule with concentrated sulphuric acid. The compound's nitrogen is quantitatively transformed into ammonium sulphate. It is then distilled with a high concentration of sodium hydroxide. The ammonia produced by this method is injected into a known volume of H_2SO_4. The chemical equations involved are shown below.

Volumetric analysis (titration against a standard alkali) is used to measure the quantity of acid that is left unused, and the amount of ammonia produced can be calculated. As a result, the percentage of nitrogen in the compound can be calculated. This approach is inapplicable to compounds with nitrogen in a ring structure, and it is also inapplicable to compounds with nitro and azo groups.

23. Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

23. Estimation of halogens

Halogens are estimated by the Carius method. In this method, a known quantity of organic compound is heated with fuming nitric acid in the presence of silver nitrate, contained in a hard glass tube called the Carius tube, taken in a furnace. Carbon and hydrogen that are present in the compound are oxidized to form CO2 and H2O respectively and the halogen present in the compound is converted to the form of AgX. This AgX is then filtered, washed, dried, and weighed.

Let the mass of organic compound be m g.

Mass of AgX formed = m1 g

1 mol of Agx contains 1 mol of X.

Therefore,

$$\text{Mass of halogen inm1 g of AgX} = \frac{\text{Atomic mass of X} \times m_1 \text{ g}}{\text{Molecular mass of AgX}}$$

$$\text{Thus, \% of halogen will be} = \frac{\text{Atomic mass of X} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}$$

Estimation of Sulphur

In this method, a known quantity of organic compound is heated with either fuming nitric acid or sodium peroxide in a hard glass tube called the Carius tube. Sulphur, present in the compound, is oxidized to form sulphuric acid. On addition of excess of barium chloride to it, the precipitation of barium sulphate takes place. This precipitate is then filtered, washed, dried, and weighed. Let the mass of organic compound be m g.

Mass of $BaSO_4$ formed = m_1 g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g of Sulphur

Therefore, m_1 g of $BaSO_4$ contains $= \frac{32 \times m_1}{233}$ g of Sulphur.

$$\text{Thus, percentage of sulphur} = \frac{32x \times m_1 \times 100}{233 \times m}$$

Estimation of phosphorus

In this method, a known quantity of organic compound is heated with fuming nitric acid. Phosphorus, present in the compound, is oxidized to form phosphoric acid. By adding ammonia and ammonium molybdate to the solution, phosphorus can be precipitated as ammonium phosphomolybdate.

Phosphorus can also be estimated by precipitating it as $MgNH_4PO_4$ by adding magnesia mixture, which on ignition yields Mg_2P2O_7.

Let the mass of organic compound be m g.

Mass of ammonium phosphomolybdate formed = m_1 g

Molar mass of ammonium phosphomolybdate = 1877 g

Thus, percentage of phosphorus $= \frac{31 \times m_1 \times 100}{1877 \times m}\%$

If P is estimated as $Mg_2P_2O_7$,

Thus, percentage of phosphorus $= \frac{62 \times m_1 \times 100}{222 \times m}\%$

24. Explain the principle of paper chromatography.

24. Paper chromatography employs the use of chromatography paper. This paper includes trapped water, which behaves as the stationary phase. The solution of the mixture is spotted on the base of this chromatography paper. The paper strip is then hung in a suitable solvent, which serves as the mobile phase. By capillary action, this solvent moves up the chromatography paper and flows over the spot during the procedure. Different component spots travel to different heights with mobile phase. The resulting paper is known as a chromatogram.

25. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

25. While testing the Lassaigne's extract for the presence of halogens, it is first boiled with dilute nitric acid. This is done to decompose NaCN to HCN and Na2S to H2S and to expel these gases. That is, if any nitrogen and sulphur are present in the form of NaCN and Na2S, then they are removed. The chemical equations involved in the reaction are represented as

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

26. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

26. Organic chemicals are covalently bonded to nitrogen, sulfur, and halogens. They must first be changed to ionic form in order to be detected. This is accomplished by combining the organic chemical with sodium metal. This is known as the "Lassaigne's test." The chemical equations used in the test are as follows:

$$Na + C + N \rightarrow NaCN$$

$$Na + S + C + N \rightarrow NaSCN$$

$$2Na + S \rightarrow Na_2\ S$$

$Na + X \rightarrow NaX$

Here, X is halogen like chlorine, bromine, iodine.

Organic compounds contain carbon, nitrogen, sulfur, and halogen.

27. Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

27. The process of sublimation is used to separate a mixture of camphor and calcium sulphate. In this process, the sublimable compound changes from solid to vapour state without passing through the liquid state. Camphor is a sublimable compound and calcium sulphate is a non-sublimable solid. Hence, on heating, camphor will sublime while calcium sulphate will be left behind.

28. Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

28. In the process of steam distillation, the organic liquid begins to boil when the total of the organic liquid's vapour pressure (p_1) and the water's vapour pressure (p_2) equals atmospheric pressure (p), i.e. $p = p_1 + p_2$. Therefore, $p_1 < p_2$

Hence, organic liquid will vapourize at a lower temperature than its boiling point.

29. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

29. CCl_4 will not give the white precipitate of AgCl on heating it with silver nitrate. This is because the chlorine atoms are covalently bonded to carbon in CCl_4. To obtain the precipitate, it should be present in ionic form and for this, it is necessary to prepare the Lassaigne's extract of CCl_4.

30. Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

30. Carbon dioxide is an acidic substance, whereas potassium hydroxide is a strong basic. As a result, when carbon dioxide combines with potassium hydroxide, potassium carbonate and water are formed. $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$ As a result, the mass of the KOH containing U-tube increases. This rise represents the amount of CO_2 created. The proportion of carbon in the organic compound can be determined based on its mass.

31. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

31. Although the addition of sulphuric acid will precipitate lead sulphate, the addition of acetic acid will ensure a complete precipitation of sulphur in the form of lead sulphate due to common ion effect. Hence, it is necessary to use acetic acid for acidification of sodium extract for testing sulphur by lead acetate test.

32. An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

32. The percentage of carbon in organic compound is 69%. It means $100\ g$ of organic compound contains $69\ g$ of carbon. So, the mass of carbon contained in $0.20\ g$ of organic compound is calculated as Mass of $C = \frac{69 \times 0.20}{100} = 0.138\ g$ of C

The molecular mass of carbon dioxide is $44\ g/mol$. Therefore, $12\ g$ of carbon is contained in $44\ g$ of CO_2. Therefore, the mass of CO_2 contained in $0.138\ g$ of carbon is calculated as Mass of $CO_2 = \frac{44 \times 0.138}{12} = 0.506\ g$

Thus, $0.506\ g$ of $CO2$ will be produced on complete combustion of $0.2\ g$ of organic compound.

The percentage of hydrogen in organic compound is 4.8%. It means $100\ g$ of organic compound contains $4.8\ g$ of hydrogen.

Therefore, the mass of hydrogen contained in $0.20\ g$ of organic compound is calculated as

Mass of $H = \frac{4.8 \times 0.20}{100} = 0.0096\ g$ of H

It is known that the molecular mass of water is $18\ g/mol$. Thus, $2\ g$ of hydrogen is contained in $18\ g$ of water. Therefore, the mass of water contained in $0.0096\ g$ of hydrogen is calculated as

Mass of $H_2O = \frac{18 \times 0.0096}{2} = 0.0864\ g$

33. A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

33. Given that, total mass of organic compound = 0.50 g

60 mL of 0.5 M solution of NaOH was required by residual acid for neutralisation.

60 mL of 0.5 M NaOH solution $= \frac{60}{2}$ mL of 0.5M H_2SO_4 = 30 mL of 0.5 M H_2SO_4

∴ Acid consumed in absorption of evolved ammonia is (50â€“30) mL = 20 mL

Again, 20 mL of 0.5 MH_2SO_4 = 40 mL of 0.5 MNH_3

Also, since 1000 mL of 1 MNH3 contains 14 g of nitrogen,

∴ 40 mL of 0.5 M NH_3 will contain $\frac{14 \times 40}{1000} \times 0.5 = 0.28\ g$ of N

Therefore, percentage of nitrogen in 0.50 g of organic compound $= \frac{0.28}{0.50} \times 100 = 56\%$

34. 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

34. Given: The mass of organic compound is $0.3780\ g$ and the mass of silver chloride formed is $0.5740\ g$. The molar mass of $AgCl$ is $143.32\ g/mol$ and the molar mass of chlorine is $35.5\ g/mol$.

One mole of silver chloride contains one mole of chlorine. So, the mass of chlorine in $0.5740\ g$ of silver chloride is calculated as

Mass of $AgCl = \frac{35.5 \times 0.5740}{143.32} = 0.1421\ g$

Thus, the percentage of chlorine is calculated as

Percentage of chlorine $= \frac{0.1421}{0.3780} \times 100\% = 37.59\%$

Hence, the percentage of chlorine is 37.59%.

35. In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

35. Total mass of organic compound = 0.468 g [Given]

Mass of barium sulphate formed = 0.668 g [Given]

1 mol of $BaSO_4$ = 233 g of $BaSO_4$ = 32 g of sulphur

Thus, 0.668 g of $BaSO_4$ contains $\frac{32 \times 0.668}{233}$ g of sulphur = 0.0917 g of sulphur

Therefore, percentage of sulphur $= \frac{0.0197}{0.468} \times 100 = 19.59\%$

Hence, the percentage of sulphur in the given compound is 19.59 %.

36. In the organic compound CH_2=CH-CH_2-CH_2-CÃ¢â€°Â¡CH, the pair of hydridised orbitals involved in the formation of: C_2-C_3 bond is:

(a) $sp - sp^2$ (b) $sp - sp^3$

(c) $sp^2 - sp^3$ (d) $sp^3 - sp^3$

36. The given organic compound is shown below.

$$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_2 - \overset{5}{C} \equiv \overset{6}{C}H$$

The hybridization of carbon atoms numbered as $1, 2, 3, 4, 5$ and 6 are sp, sp, sp^3, sp^3, sp^2, and sp^2 respectively. Therefore, the pair of hybridized orbitals involved in the formation of $C_2 - C_3$ bond is $sp - sp^3$.

37. In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$

(c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

37. In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III)

hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$$6CN^- + Fe^{2+} \longrightarrow \left[Fe(CN)_6\right]^{4-}$$

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4\left[Fe(CN)_6\right]_3}.xH_2O$$

Hence, the Prussian blue colour is due to the formation of $Fe_4[Fe(CN)_6]_3$.

38. Which of the following carbocation is most stable?

(a) $(CH_3)_3C.\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$

(c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2CH_3$

38. $(CH_3)_3\overset{+}{C}$ is a tertiary carbocation. Because of the electron-releasing effect of three methyl groups, a tertiary carbocation is the most stable carbocation. Three methyl groups increase the + I effect, which stabilizes the positive charge on the carbocation. The stability of tertiary carbocations is also due to hyperconjugation and resonance energy.

39. The best and latest technique for isolation, purification and separation of organic compounds is:

(a) Crystallisation (b) Distillation

(c) Sublimation (d) Chromatography

39. Chromatography is the most useful and the latest technique of separation and purification of organic compounds. It was first used to separate a mixture of coloured substances.

40. The reaction:

$$CH_3CH_2I + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KI$$

is classified as:

(a) electrophilic substitution

(b) nucleophilic substitution

(c) elimination

(d) addition

40. The reaction is given as: $CH_3CH_2I + KOH_{(aq)} \rightarrow CH_3CH_2OH + KI$ It shows a nucleophilic substitution reaction. The hydroxyl group of potassium hydroxide with a lone pair serves as a nucleophile, substituting iodide ion in CH_3CH_2I to produce ethanol.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